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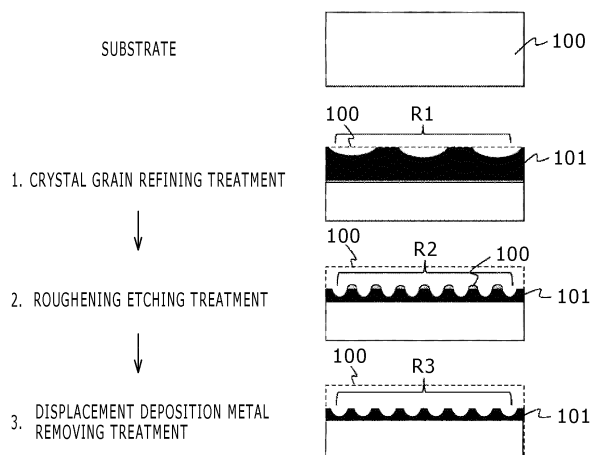
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(54) **METHOD FOR PROCESSING SURFACE OF STAINLESS STEEL, AND HEAT EXCHANGER OBTAINED USING SAME**

(57) In a surface treatment method for stainless steel, a stainless-steel surface fine-structure forming method for forming a fine irregular structure (roughened surface) having a high surface area is provided. A stainless-steel surface treatment method according to the present invention is for forming the fine structure on the surface of

stainless steel. The method includes: a first step of performing grain refining treatment for refining crystal grains in the surface of stainless steel; and a second step performed, after the first step, for roughening etching the surface of stainless steel with an etching solution.

FIG. 2



Description

Technical Field

[0001] The present invention relates to a surface treatment method for stainless steel.

Background Art

[0002] Stainless steels are excellent in strength and corrosion resistance and hence, are used in a variety of applications including architectural members, hygienic members and materials for electric appliances and the like. In recent years, a stainless steel further increased in the corrosion resistance by laminating a coating material or resin film on its surface has been often used. When laminating the stainless steel with the coating material or resin film, the surface of stainless steel must be roughened for enhancing adhesion between the stainless steel and the coating material or resin film. Surface roughening techniques for stainless steel include: blasting for physically forming an irregular surface; roughening etching for chemically or electrically forming the irregular surface; and combinations thereof. For example, Patent Literature 1 proposes a method for chemically and uniformly roughening the surface of stainless steel by using an etching solution based on sulfuric acid, chlorine ions and cupric ions. Further, Patent Literature 2 proposes a method where sandblasting is followed by chemical etching with hydrofluoric acid, nitric acid, hydrochloric acid or aqueous solution of phosphoric acid.

Citation List

Patent Literatures

[0003]

Patent Literature 1: Japanese Unexamined Patent Application Publication No. 2001-11662
Patent Literature 2: Japanese Unexamined Patent Application Publication No. Hei 5-264045

Summary of Invention

Technical Problem

[0004] According to the surface roughening technique using the etching treatment disclosed in Patent Literature 1 and the like, an irregular structure is formed by preferentially etching crystal grain boundaries. Therefore, the dimensions such as width and height of the irregular structure depend upon the crystal grain size of stainless steel. It is almost impossible to form the irregular structure in dimensions of 10 μm or less because general stainless steel has the crystal grain sizes in the range of 10 to 200 μm . Although it is possible to reduce the height of projections by reducing the etching amount, the structure is

reduced in surface area with the decrease in height. In a case where a fine structure having a height of 5 μm is formed by the surface roughening technique using the etching treatment, the structure achieves in maximum a surface area of about 14 times the area of a smooth surface. It is impossible to further increase the surface area of the fine structure.

[0005] According to Patent Literature 2, the combination of sandblasting and etching treatment provides the formation of a complicated irregular structure. However, a major irregular structure constituting a base is formed by sandblasting using abrasive grains having particle sizes on the order of 100 μm . It is therefore almost impossible to form the irregular structure in a dimension of 10 μm or less.

[0006] In this connection, an object of the present invention is to provide a stainless-steel surface treatment method for forming a fine irregular structure (roughened surface) having a high surface area on the surface of stainless steel.

Solution to Problem

[0007] While the present invention includes a plurality of means for solving the above problem, an example of such means is as follows. A stainless-steel surface treatment method according to an aspect of the present invention is for forming a fine structure on a surface of stainless steel and includes: a first step of performing grain refining treatment for refining crystal grains in the surface of stainless steel; and a second step performed, after the first step, for roughening etching the surface of stainless steel with an etching solution.

Advantageous Effects of Invention

[0008] The present invention can provide a stainless-steel surface treatment method by which a fine irregular structure (roughened surface) having a high surface area can be formed on the stainless steel.

Brief Description of Drawings

[0009]

Fig. 1 is a schematic flow chart showing a process of forming a surface fine-structure.

Fig. 2 is a group of sectional views of a substrate undergoing the process of forming the surface fine-structure.

Fig. 3 shows SEM images of surfaces and cross-sections of surface fine-structures, and surface area ratios thereof.

Fig. 4 shows the results of cross-sectional crystal observation after grain refining treatment.

Fig. 5 shows the results of passive film evaluation before and after the formation of surface fine-structure.

Fig. 6 shows the results of corrosion resistance evaluation before and after the formation of surface fine-structure.

Fig. 7 is a structure diagram of a shell and tube heat exchanger according to a second embodiment of the present invention. Description of Embodiments

[0010] The embodiments of the present invention will hereinbelow be described with reference to the accompanying drawings.

[0011] Fig. 1 is a flow chart showing the steps of a process of forming a surface fine-structure of stainless steel according to the present invention.

[0012] As shown in Fig. 1, the process of the present invention is carried out in the order of grain refining treatment (first step) and roughening etching treatment (second step). It is noted that displacement deposition metal removing treatment (third step) may be performed after the roughening etching treatment (second step) as needed.

[0013] A stainless-steel surface treatment method of the present invention for forming a fine structure on the surface of stainless steel is featured by refining crystal grains in the surface of stainless steel, followed by preferentially etching grain boundaries. Provided that R1 denotes an irregular structure formed by grain refining treatment of a first step, R2 denotes an irregular structure formed by roughening etching treatment as a second step, and R3 denotes an irregular structure formed by displacement deposition metal removing treatment as a third step, as shown in Fig. 2, a final surface fine-structure obtained according to the present invention is R2 or R3. That is, the surface fine-structure obtained according to the present invention does not include the irregular structure (R1) formed by the grain refining treatment of the first step. While the sizes of the irregular structures are arranged in ascending order $R3 < R2 < R1$, the sizes of R2 and R3 are substantially the same, suggesting that sufficiently fine irregular structures can be formed. These features assure that a fine roughened surface having a high surface area can be formed on the stainless steel.

[0014] The grain refining treatment (first step) is processing for forming a fine crystal layer in the surface by refining crystal grains in the surface of stainless steel. This fine crystal layer preferably has a thickness of 1 μm or more and grain sizes of 1 μm or less because the final surface fine-structure formed according to the present invention is highly dependent on the thickness and the grain sizes of the fine crystal layer formed by this grain refining treatment. It is noted that the general stainless steel has grain sizes of 10 μm or more. The grain refining treatment method is not particularly limited and may employ heretofore known peening treatment, grinding, turning, machining with grinder, and the like. Above all, the peening treatment is preferred which is adapted for adjustment of the thickness and grain size of the fine crystal layer according to machining conditions such as abrasive grain size and pressure.

[0015] The roughening etching treatment (second step) is processing for preferentially etching the crystal grain boundaries of the fine crystal layer formed by the first step. Therefore, the composition of a roughening etching solution preferably has strong acidity and contains chloride ions and transition metal ions capable of displacement deposition on iron. The chloride ions have an effect to destroy a passive film composed mainly of chromium oxide generated on the stainless steel surface. The chloride ions are not particularly limited. Examples of the usable chloride ions include hydrogen chloride, sodium chloride, potassium chloride, and the like. The transition metal ions capable of displacement deposition on iron have an effect to accelerate the etching of the crystal grain boundaries by inducing the displacement deposition of a metal on iron as a main component of the stainless steel so as to suppress the etching of stainless steel. Preferred transition metal ions capable of displacement deposition on iron are those having an electric potential nobler than a standard potential of iron -0.44(V) and providing high potential difference, which include copper (+0.34(V)), silver (+0.80(V)), palladium (+0.99(V)), platinum (+1.19(V)), and gold (+1.50(V)). Particularly preferred are copper ions which are less costly.

[0016] The displacement deposition metal removing treatment (third step) is processing for preferentially etching the metal deposited on the stainless steel surface in the second step. Non-selective etching treatment is less preferable because the surface fine-structure constituting the stainless steel is etched away together with the deposited metal. It is therefore important that the composition of the solution used for the displacement deposition metal removing treatment does not contain chloride ions or nitrate ions that accelerate the etching of stainless steel and has a high dissolution rate ratio for stainless steel. It is noted that the solution composition varies depending upon the type of displacement deposition metal. In a case where the displacement deposition metal is copper, a solution composition containing persulfate or hydrogen peroxide is preferred. In a case where the displacement deposition metal is gold, platinum, palladium, or silver, a solution composition containing potassium cyanide or ammonium peroxosulfate is preferred.

[0017] The third step is performed in a case where the presence of the displacement deposition metal adversely affects the fine structure on the stainless steel surface in terms of product characteristics. In a case where the surface fine-structure is required of corrosion resistance, for example, it is preferred to perform the displacement deposition metal removing treatment if the displacement deposition metal is copper which is prone to oxidation. On the other hand, the third step is omitted if the removal of the displacement deposition metal is not required, such as when even though a metal is deposited on the surface fine-structure, the displacement deposition metal concerned does not adversely affect the surface fine-structure.

(Surface/Cross-section Observation Method)

[0018] A scanning electron microscope (SEM) was used for surficial and cross-sectional observation of the surface fine-structure. The height and width of the surface fine-structure were determined from cross-sectional SEM images. In this test, out of projections shown in the cross-sectional SEM image, five projections having greater heights and widths were measured. The measured values were averaged out and the average values were identified as the height and width of the projection of the surface fine-structure.

(Surface Area Evaluation Method)

[0019] Krypton gas adsorption method was used for measuring the surface area. The measured surface area was evaluated in terms of surface area ratio on the basis of a smooth test piece not subjected to the process of forming the surface fine-structure.

(Passive Film Evaluation Method)

[0020] For passive film evaluation, surface chromium concentration was measured by Auger electron spectroscopy analysis method. The measured surface chromium concentration was evaluated in terms of surface chromium concentration ratio on the basis of the smooth test piece not subjected to the process of forming the surface fine-structure.

(Fine Crystal Layer Observation Method)

[0021] Electron Backscatter Diffraction method (EBSD) was used for observation of the fine crystal layer. OIM-Analysis commercially available from TSL Solutions Ltd. was used as a crystal orientation analysis software.

(Corrosion Resistance Evaluation Method)

[0022] A combined cycle test complying with "Neutral Salt Spray Cycle Test Method" JISK5600-7-9 was performed for evaluation of corrosion resistance. The number of test cycles was 42. The corrosion state was evaluated according to the rating number method JISZ2371 Appendix 1 (Specifications).

(Adhesion Evaluation Method)

[0023] An adhesion evaluation test was performed as follows. Polyimide (Hitachi Chemical Co., Ltd.) was applied to test pieces in a thickness of 50 μm and the polyimide film was peeled off with an adhesive tape.

First Embodiment

[0024] A first embodiment is described by way of an example where wet peening treatment was used as the

grain refining treatment (first step); a roughening etching solution containing copper ions as the transition metal ions capable of displacement deposition on iron was used in the roughening etching treatment (second step); and a displacement deposition metal removing solution containing persulfate was used in the displacement deposition metal removing treatment (third step). The test pieces were made of SUS304.

(1) Grain Refining Treatment (First Step)

[0025] The wet peening treatment used glass pellets having a diameter of about 50 μm as abrasive grains and was performed under the conditions: air pressure of 0.33 MPa and conveyance speed of 20 mm/sec. It is preferred to adjust the wet peening treatment conditions according to a required crystal grain size and a required thickness of the fine crystal layer.

(2) Roughening Etching Treatment (Second Step)

[0026] The composition of the roughening etching solution included: 500 g/l of sulfuric acid; 90 g/l of sodium chloride; and 30 g/l of cupric chloride dehydrate. The treatment was performed at a solution temperature of 40 $^{\circ}\text{C}$ for treatment time of 5 min. The treatment time may preferably be adjusted according to the etching amount required.

(3) Displacement Deposition Metal Removing Treatment (Third step)

[0027] The composition of the displacement deposition metal removing solution included: 200 g/l of sodium persulfate; and 50 ml/l of sulfuric acid which are capable of selective removal of copper, because the roughening etching solution of the second step employed copper as the transition metal ions capable of displacement deposition on iron. The treatment was performed at a solution temperature of 30 $^{\circ}\text{C}$ for treatment time of 10 min. The treatment time may preferably be adjusted according to the amount of deposited metal.

[0028] The test pieces of the first embodiment were subjected to the surficial and cross-sectional observation by SEM, the surface area evaluation and the fine crystal layer observation.

[0029] Fig. 3 shows the results of the surficial and cross-sectional observation by SEM and the surface area evaluation. It is confirmed from the surficial and cross-sectional SEM images shown in Fig. 3 that the fine structure having a width of 1 μm or less and a height of about 3 μm is formed. The surface area of this fine structure was 21 times the area of the smooth surface. This indicates that the surface fine-structure having a height of 5 μm or less and a surface area ratio of 15-fold or more can be formed on the stainless steel.

[0030] Fig. 4 shows the observation results of the fine crystal layer after the wet peening treatment. The fine

crystal layer was formed in a depth of about 7 μm from the stainless steel surface and has a grain size of about 0.8 μm . This indicates that the fine crystal layer having a grain size of 1 μm or less and a thickness of 1 μm or more can be formed in the stainless steel surface.

Second Embodiment

[0031] In this embodiment, a fine structure was formed on the surface of a test piece under the same conditions as those of the first embodiment except that the treatment time of the roughening etching treatment (second step) in the first embodiment was changed to 3 min. The test pieces of the second embodiment were subjected to the surficial and cross-sectional observation by SEM and the surface area evaluation. Fig. 3 shows the results of the surficial and cross-sectional observation by SEM and the surface area evaluation. It is confirmed from the surficial and cross-sectional SEM images of Fig. 3 that the fine structure having a width of 1 μm or less and a height of about 1 μm is formed. The surface area of this fine structure is 15 times the area of the smooth surface. This indicates that the dimensions or surface area of the fine structure can be adjusted by varying the condition of the wet peening treatment or the etching treatment. As compared with the first embodiment, the fine structure is decreased in the surface area ratio because of the decreased height of the structure. However, even with the height of 1 μm , the fine structure can achieve the 15-fold increase in the surface area ratio.

Third Embodiment

[0032] In this embodiment, the test pieces prepared in the first embodiment were subjected to the passive film evaluation, the corrosion resistance evaluation and the adhesion evaluation. The results are described as below.

[0033] Fig. 5 shows the results of the passive film evaluation after the formation of the surface fine-structure. It is confirmed that the chromium concentration in the stainless steel surface increased by a factor of 1.5 times over the level before the formation of the surface fine-structure. This is attributable to a fact that chromium dispersed in the stainless steel remains in the stainless steel surface.

[0034] Fig. 6 shows the results of the corrosion resistance evaluation before and after the formation of the surface fine-structure. The stainless steel before the formation of the surface fine-structure had a rating number of 6 (corrosion area 0.5 to 1.0%) while the stainless steel after the formation of the surface fine-structure had a rating number of 10 (corrosion area 0.0%). It was thus confirmed that the stainless steel was improved in the corrosion resistance by forming the surface fine-structure by the surface treatment method of the embodiment. Judging from the results of the passive film evaluation, the improved corrosion resistance is considered to be the result of the surface chromium concentration in-

creased by the surface fine-structure forming process.

[0035] The results of the adhesion evaluation after the surface fine-structure forming process indicate no separation of the polyimide film. That is, high adhesion with the film can be achieved by applying the surface fine-structure forming process to the stainless steel.

[Comparative Example 1]

[0036] Comparative Example 1 is described by way of an example where wet blasting treatment was used as a method for forming the surface fine-structure on the stainless steel. The test pieces were made of SUS304.

[0037] As for the conditions of the wet blasting treatment, polygonal alumina particles having a particle size of about 15 μm were used as the abrasive grains under air pressure of 0.2 MPa.

[0038] The test pieces of Comparative Example 1 were subjected to the surficial and cross-sectional observation by SEM and the surface area evaluation. Fig. 3 shows the results of the surficial and cross-sectional observation by SEM and the surface area evaluation. It is confirmed from the surficial and cross-sectional SEM images of Fig. 3 that the fine structure having a width of 2 to 3 μm and a height of about 0.5 μm is formed in Comparative Example 1. The surface area of the structure of Comparative Example 1 is 3 times the area of the smooth surface.

[0039] The results of the adhesion evaluation after the surface fine-structure forming process indicate the separation of the polyimide film on the whole area.

[Comparative Example 2]

[0040] Comparative Example 2 is described by way of an example where roughening etching treatment was used as the method for forming the surface fine-structure on the stainless steel. The test pieces were made of SUS304.

[0041] The conditions of the roughening etching treatment were the same as those of the first embodiment. The solution composition includes: 500 g/l of sulfuric acid; 90 g/l of sodium chloride; and 30 g/l of cupric chloride dehydrate. The treatment was performed at a solution temperature of 40°C for treatment time of 5 min.

[0042] The test pieces of Comparative Example 2 were subjected to the surficial and cross-sectional observation by SEM and the surface area evaluation. Fig. 3 shows the results of the surficial and cross-sectional observation by SEM and the surface area evaluation. It is confirmed from the surficial and cross-sectional SEM images of Fig. 3 that the fine structure having a width of 2 to 5 μm and a height of about 3 μm is formed in Comparative Example 2. The surface area of the structure of Comparative Example 2 is 10 times the area of the smooth surface.

[0043] The results of the adhesion evaluation after the surface fine-structure forming process indicate a partial separation of the polyimide film.

[0044] The first and second embodiments are com-

pared with Comparative Examples 1 and 2. The surface fine-structure formed by the wet blasting treatment of Comparative Example 1 is poor in fineness, having a slightly larger distance between fine structures, which may depend upon the size of the abrasive grains. On the other hand, the surface fine-structure formed by the roughening etching treatment of Comparative Example 2 has large widths, which depend upon the size of crystal grains of the substrate because the treatment etches the crystal grain boundaries. That is, it is almost impossible for the conventional surface structure forming methods including the wet blasting treatment and the roughening etching treatment to form, on stainless steel, the surface fine-structure having a height of 5 μm or less and a surface area ratio of 15-fold or more.

Fourth Embodiment

[0045] Next, description is made on the examples of application of the stainless steel having the surface fine-structure formed by the surface treatment method of the present invention. A preferred example of the application of the stainless steel formed with a fine irregular structure having a high surface area is an air-cooled heat exchanger performing heat exchange via gas. By applying the stainless steel subjected to the inventive surface treatment to a heat transfer part of the air-cooled heat exchanger, the heat transfer part is increased in the surface area, and heat transfer performance is improved. Because of an extremely fine irregular structure, the heat exchanger is decreased in pressure loss, thus achieving a high heat transfer accelerating effect.

[0046] In this embodiment, a shell and tube heat exchanger employing a heat transfer tube made of the stainless steel formed with the surface fine-structure by the surface treatment method of the first embodiment was evaluated for the heat transfer performance.

[0047] Fig. 7 is a structure diagram of a shell and tube heat exchanger according to a fourth embodiment of the present invention. A circular or polygonal shell 200 is provided with tube plates 202 on opposite sides thereof for supporting heat transfer tubes 201 as the heat transfer part. The tube plate 202 includes a plurality of holes arranged in a staggered fashion and penetrated by the heat transfer tubes 201. The heat transfer tubes 201 are inserted through these tube holes and secured to the tube plates 202 at opposite ends thereof. The length of the heat transfer tube 201 is equal to or more than 25 times the characteristic length D of flow. The characteristic length D of the flow along the tube group of the embodiment is defined by a hydraulic equivalent diameter. In a case where the air flow is turbulent, the heat transfer performance can be further improved by defining the length of the heat transfer tube 201 to be equal to or more than 25 times the characteristic length D of flow.

[0048] A fine structure 203 is formed on an outside surface of the heat transfer tube 201. Air 204, as a low-temperature fluid, enters the heat exchanger through a

nozzle 205 disposed at a side of a lower part of the heat exchanger. The air moves up around the heat transfer tubes 201, exchanging heat with water vapor as a high-temperature fluid via heat transfer tube walls. The water vapor 206 as the high-temperature fluid enters the heat exchanger through a nozzle 207 at a top of the heat exchanger and flows through a water chamber 208 at the top of the heat exchanger and down through the heat transfer tubes 201. The water vapor 206 is condensed into compressed water by heat exchange with the air 204 as the low-temperature fluid via the heat transfer tube walls. The compressed water flows through a water chamber at a bottom of the heat exchanger so as to flow out of the heat exchanger through a nozzle at the bottom of the heat exchanger.

[0049] As a result of the application of the stainless steel formed with the surface fine-structure by the surface treatment method of the first embodiment to the heat transfer tube 201, the heat exchanger of the embodiment can be increased by about 6% in the heat transfer performance compared with that of a shell and tube heat exchanger using stainless steel subjected to no surface treatment. As described above, the application of the stainless steel formed with the surface fine-structure by the inventive surface treatment method provides for the increase in the heat transfer performance without increasing the number of heat transfer tubes. Namely, the present invention permits the reduction of the number of heat transfer tubes when achieving a desired heat transfer performance, which leads to the cost reduction of heat exchanger.

[0050] For comparison, the heat transfer tube 201 was made of the stainless steel formed with the surface fine-structure by the surface treatment method of Comparison Example 2. The resultant heat exchanger was increased by about 2.5% in the heat transfer performance compared with that of the shell and tube heat exchanger using the stainless steel subjected to no surface treatment. It was thus confirmed that the heat transfer tube 201 was improved further in the heat transfer performance as the surface area ratio thereof increased.

[0051] As for the height of the fine structure, the lower the height, the better is the fine structure as long as the surface area thereof is constant. This is because the pressure loss increases with the increase in the height of the fine structure. Although the fine structure having a height beyond a boundary layer can provide the high heat transfer accelerating effect, this effect is traded off against the increase in the pressure loss. This may result in a case where the increased pressure loss wholly cancels out the improvement in heat transfer performance. The boundary layer means a thin layer which exists in vicinity of a contact surface with gas and at which gas viscosity is non-negligible (or which is strongly affected by gas viscosity). The thickness of the boundary layer varies depending upon the specifications of the heat exchanger, namely a variety of requirements such as gas flow rate, mode of gas flow, configurations of the heat

transfer part, and the like. From the standpoint of reliably reducing the pressure loss, the fine structure desirably has the lower height and the larger surface area ratio. The surface treatment method of the present invention makes it possible to form the surface fine-structure having the height of 5 μm or less and the surface area ratio of 15-fold or more, which has been impracticable for the conventional method. Therefore, the heat transfer performance higher than the conventional level can be achieved by applying the stainless steel formed with this fine structure on its surface to the heat transfer part of the heat exchanger.

[0052] As shown in Figs. 5 and 6, the stainless steel is increased in the surface chromium concentration, featuring excellent corrosion resistance. Accordingly, the stainless steel is preferably applied to the heat transfer part of the heat exchanger required of corrosion resistance.

[0053] While the fourth embodiment has been described by way of the example of the shell and tube heat exchanger, the heat exchanger to which the present invention is applicable is not limited to this. The present invention can be implemented in a heat exchanger which performs heat exchange by making contact with a gas and in which the heat transfer part making contact with the gas is made of the stainless steel. Examples of such a heat exchanger include: a fin-type heat exchanger (heat sink) for power semiconductor; a cross-fin type heat exchanger for air conditioner or automotive radiator; and the like.

List of Reference Signs

[0054]

100: STAINLESS STEEL
 101: FINE CRYSTAL LAYER
 102: DISPLACEMENT DEPOSITION METAL
 R1: IRREGULAR STRUCTURE AFTER GRAIN REFINING TREATMENT
 R2: IRREGULAR STRUCTURE AFTER ROUGHENING ETCHING TREATMENT
 R3: IRREGULAR STRUCTURE AFTER DISPLACEMENT DEPOSITION METAL REMOVING TREATMENT
 200: SHELL
 201: HEAT TRANSFER TUBE
 202: TUBE PLATE
 203: FINE STRUCTURE
 204: AIR
 205: NOZZLE
 206: WATER VAPOR
 207: NOZZLE
 208: WATER CHAMBER

Claims

1. A stainless-steel surface treatment method for forming a fine structure on a surface of stainless steel comprising:
 - a first step of performing grain refining treatment for refining crystal grains in the surface of stainless steel; and
 - a second step performed, after the first step, for roughening etching the surface of stainless steel with an etching solution.
2. The stainless-steel surface treatment method according to Claim 1, wherein the grain refining treatment is any one of peening treatment, machining, and grinding.
3. The stainless-steel surface treatment method according to Claim 1 or 2, wherein a fine crystal layer formed in the surface of stainless steel by the grain refining treatment of the first step has a thickness of 1 μm or more, and the crystal grains of the fine crystal layer have grain sizes of 1 μm or less.
4. The stainless-steel surface treatment method according to Claim 1, wherein the roughening etching treatment of the second step is to preferentially etch grain boundaries in the surface of stainless steel.
5. The stainless-steel surface treatment method according to Claim 1, wherein the etching solution contains chloride ions and transition metal ions having an electric potential nobler than a standard potential of iron, and has acidity.
6. The stainless-steel surface treatment method according to Claim 5, wherein the transition metal ions include any one or more of copper, silver, palladium, gold and platinum.
7. The stainless-steel surface treatment method according to Claim 4, further comprising a third step performed, after the second step, for removing a displacement deposition metal deposited on the surface of stainless steel by the etching treatment.
8. The stainless-steel surface treatment method according to Claim 7, wherein in the third step, the displacement deposition metal is etched away with a metal removing solution hardly dissolving stainless steel and preferentially dissolving the displacement deposition metal.
9. The stainless-steel surface treatment method according to Claim 8, wherein the displacement deposition metal is copper, and the metal removing solution contains one of persulfate and hydrogen perox-

ide.

10. The stainless-steel surface treatment method according to Claim 8, wherein the displacement deposition metal is any one of silver, palladium, gold, and platinum, and the metal removing solution contains one of potassium cyanide and ammonium peroxo-sulfate. 5
11. A stainless steel material which is prepared by the stainless-steel surface treatment method according to any one of Claims 1 to 10, the stainless steel material having a fine structure portion, on its surface, which has a height of 5 μm or less and a surface area equal to or more than 15 times an area of a smooth surface. 10 15
12. A heat exchanger comprising a heat transfer part for performing heat exchange by making contact with a gas, wherein the heat transfer part making contact with the gas is made of a stainless steel having a fine structure portion, on its surface, which has a height of 5 μm or less and a surface area equal to or more than 15 times an area of a smooth surface. 20 25
13. The heat exchanger according to Claim 12, wherein crystal grains in the fine structure portion of the heat transfer part have grain sizes of 1 μm or less.
14. The heat exchanger according to Claim 12, wherein a surface chromium concentration of the fine structure portion of the heat transfer part is equal to or more than 1.5 times the chromium concentration in a surface of the heat transfer part which is free from the fine structure portion. 30 35
15. The heat exchanger according to Claim 12, wherein the surface fine-structure of the heat transfer part is formed by the stainless-steel surface treatment method according to any one of Claims 1 to 10. 40

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FIG. 1

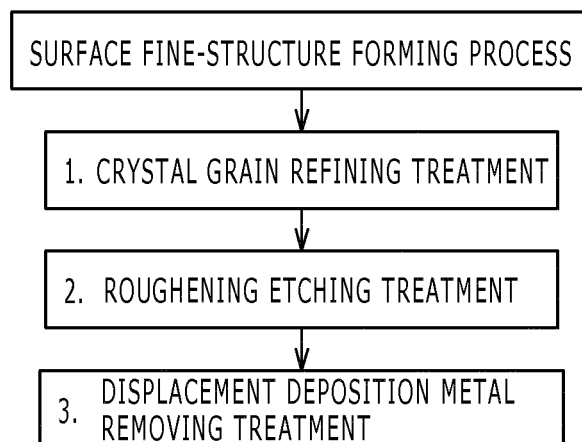


FIG. 2

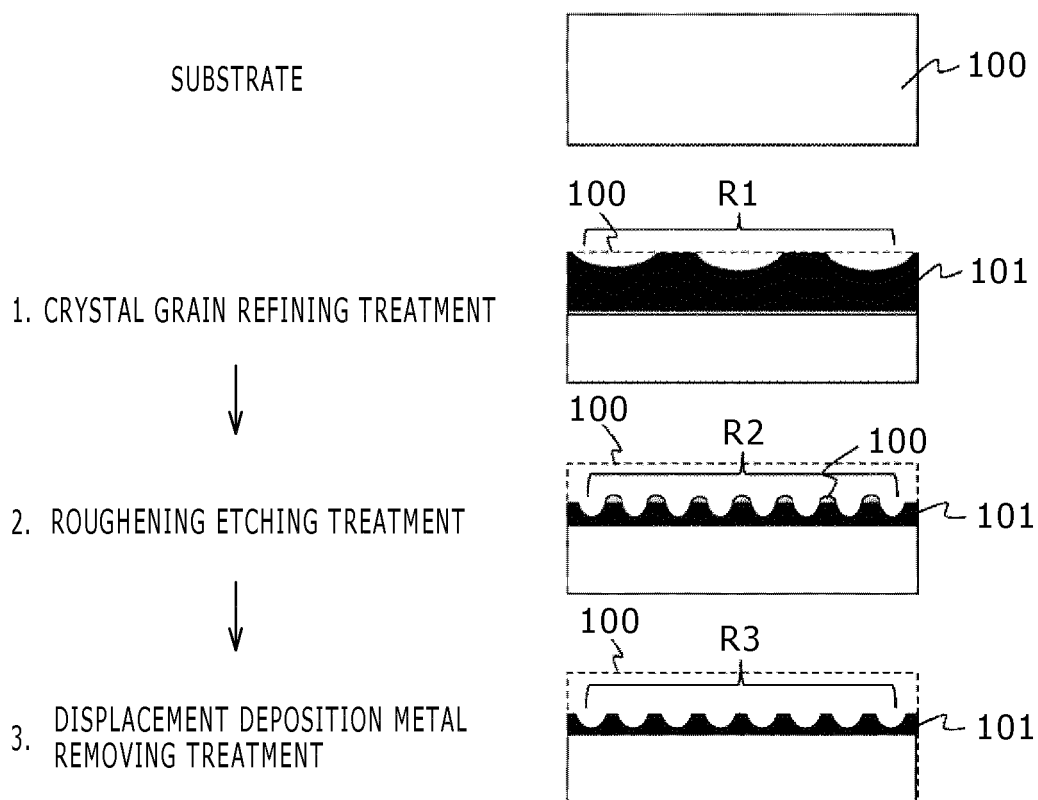


FIG. 3

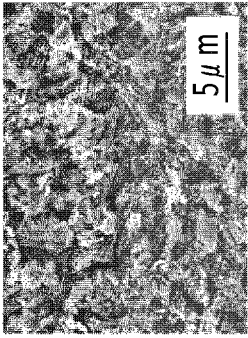
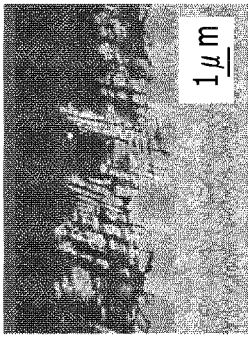
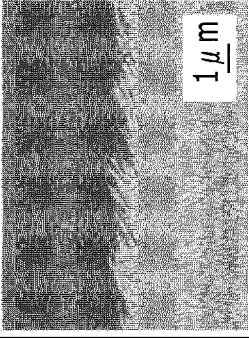
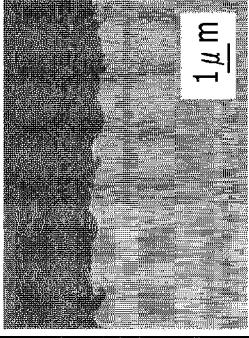
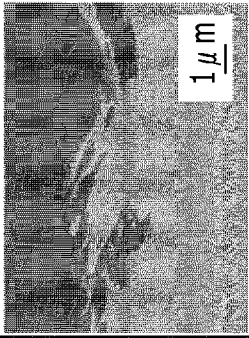
	FIRST EMBODIMENT	SECOND EMBODIMENT	COMPARATIVE EXAMPLE 1	COMPARATIVE EXAMPLE 2
SURFACE				
CROSS-SECTION				
STRUCTURE HEIGHT	ABOUT 3.0 μm	ABOUT 1.0 μm	ABOUT 0.5 μm	ABOUT 3.0 μm
SURFACE AREA RATIO	21-FOLD	15-FOLD	3-FOLD	10-FOLD

FIG. 4

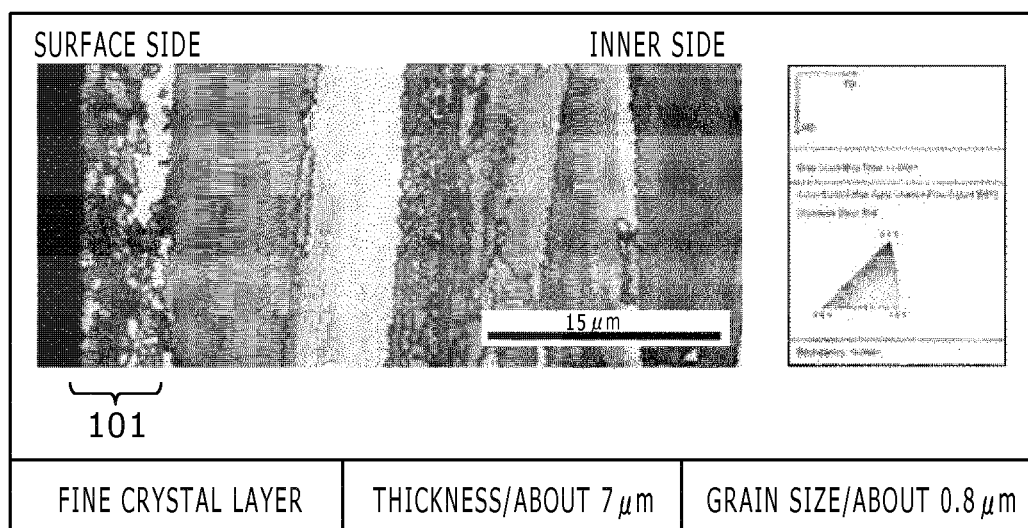


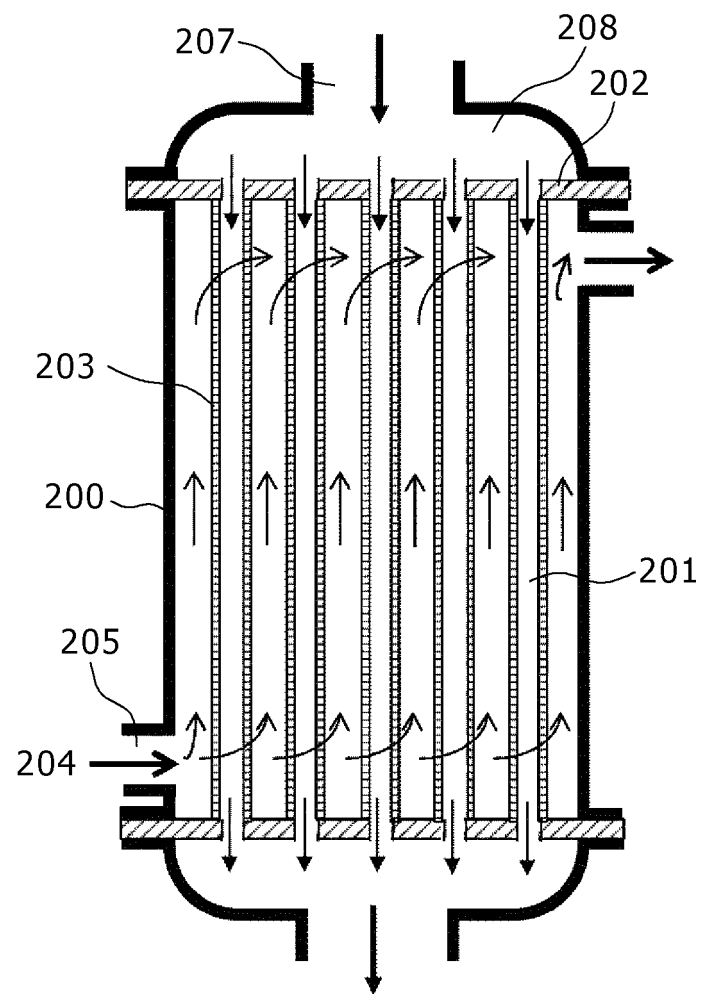
FIG. 5

	BEFORE FORMATION OF SURFACE FINE-STRUCTURE	AFTER FORMATION OF SURFACE FINE-STRUCTURE
SURFACE CHROMIUM CONCENTRATION RATIO	1	1.5

FIG. 6

	BEFORE FORMATION OF SURFACE FINE-STRUCTURE	AFTER FORMATION OF SURFACE FINE-STRUCTURE
RATING NUMBER	6	10
CORROSION AREA	0.5~1.0%	0.0 (%)

FIG. 7



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/073606

A. CLASSIFICATION OF SUBJECT MATTER

C23F1/28(2006.01)i, B24C1/06(2006.01)i, C21D7/06(2006.01)i, C23F1/00
(2006.01)i, F28F1/12(2006.01)i, F28F21/08(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23F1/28, B24C1/06, C21D7/06, C23F1/00, F28F1/12, F28F21/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

JSTPlus (JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 55-122872 A (Nisshin Steel Co., Ltd.), 20 September 1980 (20.09.1980), entire text (Family: none)	1-15
A	JP 2009-68079 A (Sumitomo Metal Industries, Ltd.), 02 April 2009 (02.04.2009), entire text (Family: none)	1-15
A	JP 8-218151 A (Nisshin Steel Co., Ltd.), 27 August 1996 (27.08.1996), entire text (Family: none)	1-15

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search
25 November, 2014 (25.11.14)

Date of mailing of the international search report
02 December, 2014 (02.12.14)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2001011662 A [0003]
- JP 5264045 A [0003]